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Full Length Article

Magneto-dielectric properties of doped ferrite based nanosized ceramics over very high frequency range

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ABSTRACT

In the present study, indium doped nano sized nickel zinc cobalt based ferrite ceramics with composition $Ni_{0.5}Zn_{0.3}Co_{0.2}In_xFe_{2-x}O_4$ (x = 0.2 and 0.4) were synthesized by a co-precipitation technique. Powdered sample has been pre-sintered at 800 °C, pressed into toroids and finally sintered at 1000 °C. The single phase formation of the presintered powder has been confirmed by X ray diffraction (XRD). The average particle size of the presintered powder has been estimated by field emission scanning electron microscope (FESEM) and found to be about ~60 nm for x = 0.2 and ~80 nm at x = 0.4. The electromagnetic characterization has been made using vector network analyzer. High value of permeability (17.3 and 15.2 for x = 0.2 and 0.4 respectively) with low magnetic loss tangent of 10^{-1} order were obtained. Permittivity of 8.2 and 10, and dielectric loss tangent of the order of 10^{-2} were also achieved. With the measured electromagnetic parameters, miniaturization factor of 12.32 and normalized characteristic impedance close to unity (1.23) were obtained up to 100 MHz frequency. These fascinating parameters definitely propose $Ni_{0.5}Zn_{0.3}Co_{0.2}In_{0.4}Fe_{1.6}O_4$ ceramics as a substrate material for miniaturized antenna in very high frequency band. Possible reasons and mechanisms of electromagnetic properties for different concentrations of indium are discussed in the paper.

1. Introduction

Continuous advancement in the research field of materials science is producing new and innovative materials. This is resulting in either up gradation and advancement of existing products and technologies or bringing new technologies for the development of our society and environment, directly or indirectly [1,2]. Among various materials, nano ferrites attracted the attention of researchers, scientists and technologists due to their wide range of applications in the field of electronics, communication, drug delivery, sensors, actuators etc. [3–8]. Considerable efforts have been made toward miniaturization of electronics and radio frequency (RF) circuits [9–12]. In electronics, size of antenna is a major bottleneck in further reduction in the size of communication packages at very high frequency (VHF) band. For space borne and defense applications, the constraint is on small form factor i.e. reduction in volume, rugged and long shelf life, with no deterioration in performance [13–15]. The size of an antenna, being proportional to the half wavelength, increases drastically at low frequencies, for its practical application in portable, mobile and size constraint applications [16].

Microstrip antenna due to its inherent advantages of planer structure, conformal to any surface, small size, low cost and ease of fabrication have been a subject of research interest over the last many years [17–22]. Scientists have investigated a variety of high dielectric materials and various topologies to miniaturize the antenna size [23–28]. High dielectric constant substrate materials can reduce the size, but suffers from two disadvantages: (i) field remains highly concentrated in high permittivity medium and (ii) decrease in characteristic impedance of substrate material results in impedance mismatch, hence, resulting in an antenna with low efficiency. These limitations and disadvantages can be overcome by loading antenna with magneto-dielectric materials [29–31]. These are engineered materials having both dielectric and magnetic properties. The properties can be suitably tailored with proper selection of ingredients, chemicals, synthesis process and proper doping for its

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effective use as substrate for microstrip antenna [32,33]. Miniaturization factor for microstrip antenna is a function of permittivity and permeability of substrate material and is given by Eq. (1).

$$n = \sqrt{(\mu_r \times \varepsilon_r)} \quad (1)$$

where n is miniaturization factor, μ_r is relative permeability and ε_r is relative permittivity of the substrate material. Hence, using moderate value of permittivity and permeability, the size of an antenna can be reduced significantly. High permeability substrate adds to the inductance, reducing the effect of capacitance and thereby reducing the problem of field confinement. Characteristic impedance of the substrate material ($Z_i = Z_0\sqrt{(\mu_r/\varepsilon_r)}$) should be close to characteristic impedance of the surrounding medium (Z_0) for proper impedance matching [34–37]. These ceramic materials also have high electrical resistivity, good chemical stability, do not absorb moisture, and therefore, do not show performance degradation over their useful life.

Among magneto-dielectric materials, it is the versatility of application and ease of preparation that makes Nickel–Zinc a very important material from research as well as production point of view. Significant work has been done to understand and characterize Ni-Zn soft ferrites [38–40]. Ni-Zn ferrite applications are limited to low frequencies only. To increase the operational frequency, effect of various dopants like cobalt, aluminum, copper, barium, indium, strontium etc. had been studied [41–44]. Doping of cobalt, due to its high positive crystalline anisotropy and due to it being a fast relaxer, is preferred for high frequency application. Since indium has larger ionic radii than Fe ion, its substitution can lead to expansion of cell and may result in high permeability. To further get high and consistent permeability in VHF region, effect of substitution of indium with Fe ion is analyzed in this present research. Wet chemical method is preferred to synthesize the ferrite material as it adds flexibility in varying the stoichiometry of the base materials [45–47]. Since the suitably tailored structural and electromagnetic properties of doped Ni-Zn soft ferrites make them a potential candidate for miniaturized microstrip antenna in space, defense and communication industry at VHF frequency region, the same is chosen for the present research work.

2. Experimental details

2.1. Synthesis and characterization

$Ni_{0.5}Zn_{0.3}Co_{0.2}In_xFe_{(2-x)}O_4$ spinel ferrite was synthesized by a co-precipitation method from nickel chloride, zinc chloride, cobalt (III) chloride, iron (III) chloride, indium chloride and sodium hydroxide (Merck/Aldrich make with purity greater than 99%). These ingredients were mixed in stoichiometric proportion and processed. Two samples for x = 0.2 (sample 1) and x = 0.4 (sample 2) were prepared. The solution was stirred with a magnetic stirrer and was dried for 12 h in a furnace at 200 °C, to obtain nanosized ferrite powder. The powder was pre-sintered at 800 °C for 4 h. The experimental details are explained elsewhere [48–50]. Structural characterization on the pre-sintered powder samples was done by X-ray diffraction (XRD) using Rigaku Geiger Diffractometer with a step scan of 0.02, 5 °C/min from 25° < 2θ < 70° Cu K(alpha) radiation having wavelength of 1.54 Å. Scanning electron microscope (SEM) images were taken (Model: EVO-50, Make: ZEISS) for the powdered samples. For electromagnetic characterization, toroidal pellets with an internal diameter of 3.2 mm and external diameter of 7 mm were prepared with poly vinyl alcohol as binder, die and hydraulic press. Measurements were done using vector network analyzer (VNA) (Model No. E5071C, make: Agilent). Pellets for both the samples were loaded one by one into suitable test fixture connected to VNA through APC 7 connector. Relative complex permittivity and relative complex permeability values were obtained directly from the measurements of transmission and reflection parameters on the samples from material measurement software of Agilent using coaxial line method. Measurement was done in 10 MHz to 400 MHz frequency band. The small air gap between the pellet and the coaxial line was taken cared of by gap correction feature of the material measurement software.

3. Results and discussion

Fig. 1 shows the XRD patterns of $Ni_{0.5}Zn_{0.3}Co_{0.2}In_{0x}Fe_{(2-x)}O_4$ (for x = 0.2 and 0.4) for samples presintered at 800 °C. The peaks observed at (220), (311), (400), (420), (511) and (440) are unique signature of cubic spinel ferrite. The XRD result, without any extra peaks, indicates the formation of uniform material without any unreacted constituents. Formation of single phase nano particles was confirmed from broadening of the peak. With increase in indium concentration from x = 0.2 to x = 0.4, a sharp increase in the intensity of most prominent peaks (311) was observed. This is attributed to the crystalline nature of spinel ferrite. Average crystallite size is obtained from (311), (440), and (511) peaks by Scherrer's formula given by Eq. (2).

$$d = \frac{0.9\lambda}{(w - w_1)\cos\theta} \quad (2)$$

where d is the diameter of the crystallite, w and w_1 are the half intensity width of the peak with maximum orientation and instrumental broadening, λ is the x-ray wavelength (0.154 nm), and θ is Bragg's angle of reflection. Average crystallite size of 60 nm was obtained at x = 0.2 and it increases with indium ion concentration to 65 nm at x = 0.4. The lattice parameter increases with increase in doping concentration and hence the volume also increased slightly as calculated in Table 1. This may be attributed to the fact that indium ions are effective in replacing Fe^{3+} ions. Since the size of In^{3+} ion (0.91 Å) is higher than that of Fe^{3+} (0.67 Å), it is expected that doping of indium leads to expansion of unit cell [51]. The XRD pattern obtained for the above samples matches closely with PDF card number 00–008-0234 for NZFO using MATCH software.

Fig. 2(a) and (b) shows SEM image of the powdered samples presintered at 800 °C (for In^{3+} concentration of x = 0.2 and x = 0.4). The images confirm the formation of nano particles with an average size of about ~60 nm for x = 0.2 and ~80 nm at x = 0.4. Some agglomeration was also observed in the powder sample; however, the agglomeration reduces with the formation of pellets as can be seen in Fig. 2(a) and (b). With an increase in indium concentration, the powder (sample-2) became densely packed. The difference in

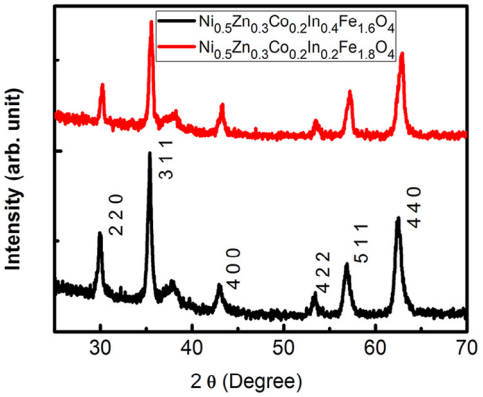

Fig. 1. X ray diffraction image of $Ni_{0.5}Zn_{0.3}Co_{0.2}In_xFe_{(2-x)}O_4$ for (x = 0.2 and 0.4) nano ferrite.